

Catalytic NO–H₂–O₂ reaction over Pt/Mg–Al–O prepared from PtCl₆^{2–} - and Pt(NO₂)₄^{2–} -exchanged hydrotalcites

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Abstract

The catalytic NO–H₂–O₂ reaction at low temperatures (50–130 °C) has been investigated over Pt-supported Mg–Al binary oxides, which were prepared from PtCl₆^{2–} and Pt(NO₂)₄^{2–}-exchanged hydrotalcite(HT)-like compounds by heating at 600 °C in H₂. Although the NO_x conversion of both catalysts was similarly high (>80%) at around 70 °C, the Pt(NO₂)₄^{2–}-HT catalyst exhibited the higher selectivity to N₂ (53% N₂ and 47% N₂O), compared to 12% N₂ and 88% N₂O for the PtCl₆^{2–}-HT catalyst. The XANES/EXAFS spectroscopy showed that Pt prepared from PtCl₆^{2–}-HT is partly oxidized due to the coordination of residual chlorides, whereas Pt(NO₂)₄^{2–}-HT yielded highly dispersed metallic Pt. Because of the presence of chloride strongly bound to Pt, the oxidative NO adsorption as NO₂/NO₃ was inhibited for PtCl₆^{2–}-HT. The improved N₂ selectivity with an increase of oxidative NO adsorption is in accord with the catalytic property of Na–Pt/ZSM-5 in our previous work [M. Machida, T. Watanabe, Appl. Catal. B: Environ. 52 (2004) 281.], suggesting that the N₂ would be formed *via* NO₂/NO₃ intermediates.

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1. Introduction

In the last decade, the catalytic NO–H₂ reaction has been investigated using various oxide supported Pt catalysts in the presence of excess O₂ at low temperatures (≤100 °C) [1–9]. According to our previous report [6–9], the catalytic NO–H₂–O₂ reaction is affected by acidic/basic characters of oxide supports. Although acidic and/or amphoteric oxides (SiO₂, ZrO₂, Al₂O₃, ZSM-5, SiO₂–Al₂O₃, TiO₂–ZrO₂, etc.) are rather effective for the NO reduction at lower temperatures, considerably more N₂O than N₂ is produced. For instance, the reaction over Pt–ZSM-5 in a stream of 0.08% NO, 0.28% H₂, 10% O₂, and He balance yielded N₂ with less than 10% selectivity, which could not be increased by changing Pt loading or H₂ concentration in the gas feed [8]. On the other

hand, the activity of Pt is decreased by the use of oxide supports with a higher basicity (CeO₂ and La₂O₃). A moderate basicity is required for the oxidative NO adsorption as NO₂/NO₃ species, but a high basicity inhibits catalytic H₂ activation. Thus, a catalyst having both moderate acidic and basic sites seems to be effective in promoting the reaction between NO_x and activated hydrogen in the presence of Pt. On this concern, Mg–Al oxides formed from hydrotalcite-like compounds (HT) are promising because of their moderate acid and base characters.

The HT compound is known as a double-layered hydroxide consisting of brucite-type (Mg(OH)₂) sheets where a part of Mg²⁺ is replaced by Al³⁺. The resulting positive charge is compensated by exchangeable anions located in the interlayer space containing water molecules. The thermal decomposition leads to the phase transformation from HT phase to amorphous Mg–Al oxides with a high porosity and with acid/basic characters. Because of these advantages, HT has been investigated as precursors for the metal-loaded porous catalysts [10–13]. Recently, we have reported the catalyst preparation by ion-exchanging HT (Mg_{0.74}Al_{0.26}(OH)₂(NO₃)_{0.26}·nH₂O) and subsequent heating in H₂ [14–16]. In the heating process, Pt species

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in the interlayer promotes the reaction between H₂ and interlayer NO₃⁻ to yield N₂ so as to give rise to a large surface area (>200 m² g⁻¹) at as low as ca. 200 °C. The resulting solid possesses thermally stable and highly dispersed Pt particles that should be interesting as a catalyst.

The objective of this work is to study the activity and selectivity of Pt supported catalysts, which is prepared from two anionic Pt-complex (PtCl₆²⁻ and Pt(NO₂)₄²⁻)-exchanged HT precursors. The correlation between the physical and chemical properties of these catalysts and their activity and selectivity for the NO–H₂–O₂ reaction is of particular interest for the development of selective deNO_x catalyst working at near room temperature.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like compound, Mg_{0.74}Al_{0.26}(OH)₂(NO₃)_{0.26}·*n* H₂O, was prepared by the co-precipitation method [14]. Mg(NO₃)₂·6H₂O (14.8 mmol) and Al(NO₃)₃·9H₂O (5.2 mmol) were dissolved into a distilled water (20 mL) and resulting mixed solution was added dropwise into NH₃ aqueous solution (1 M, 100 mL) with vigorous stirring at room temperature. The precipitate was centrifuged, washed with distilled water and then dried under reduced pressure overnight. The powder thus obtained was exchanged in aqueous solutions of K₂PtCl₆ or K₂Pt(NO₂)₄ at room temperature for 24 h to obtain PtCl₆²⁻- and Pt(NO₂)₄²⁻-exchanged HTs, which are abbreviated as Pt_c-HT and Pt_n-HT, respectively. As exchanged phases were washed with distilled water, dried under reduced pressure and heated at 600 °C in a flow of H₂ for 2 h to yield 1 wt% Pt-loaded catalysts.

2.2. Characterization

Crystal phases were determined by powder X-ray diffraction (XRD, Rigaku Multiflex) using monochromated Cu Kα radiation (30 kV, 30 mA). Chemical composition was determined using an energy disperse X-ray fluorescence measurement (Horiba MESA-500 W). Specific surface area was calculated by BET method from N₂ adsorption isotherm measured at 77 K. Pt dispersion was measured by H₂–O₂ titration using a pulsed flow technique at room temperature, as indicated in a previous paper [16]. The number of Pt atoms exposed on surface (*n*_{Pt_s}) was calculated on assuming the ratio, *n*_{H₂}/2*n*_{Pt_s}, to be unity. Pt dispersion (*D*_{Pt}) is defined as *n*_{Pt_s}/*n*_{Pt}, where *n*_{Pt} is the number of total Pt atoms on the catalyst.

Measurement of X-ray absorption spectra of Pt at the L_{III} edge for Pt_c-HT and Pt_n-HT after heating at 600 °C in H₂ was performed on the BL-10B of Photon Factory, High Energy Accelerator Research Organization at Tsukuba (Proposal #2004G088). Injection beam energy was 2.5 GeV and ring current was 300–450 mA. A Si (3 1 1) channel-cut monochromator was used. Pt L_{III}-edge spectra were recorded at room temperature in a transmission mode using an ionization chambers filled with 85% N₂ balanced with Ar for an incident

beam and of 100% Ar for a transmitted beam. To adjust an absorbance at the edge energy for the XAFS measurement, samples were pelletized after its volume was adjusted by polyethylene powder. The XAFS data were processed by a REX 2000 program (Rigaku). The EXAFS oscillation was extracted by fitting a cubic spline function through the post edge region. Pt foil, K₂PtCl₆ and PtO₂ were used as references in order to extract the amplitude and phase shift function for Pt–Pt, Pt–Cl and Pt–O bonds.

2.3. Adsorption and catalytic measurement

NO adsorption and steady state NO–H₂–O₂ reaction were carried out in a conventional flow reactor equipped with a water-cooled infrared image furnace. A granulated catalyst (10–20 mesh, 0.2 g) was fixed by quartz wool in a Pyrex glass tube (4 mm i.d.). The catalyst was pretreated at 400 °C in 5% H₂/He flow for 1 h before use. Breakthrough curves of NO_x adsorption were measured in a flowing gaseous mixture of 0.16% NO, 10% O₂, balanced with He supplied at 0.24 s g cm⁻³. The concentration of NO_x (NO + NO₂) in the effluent was measured by using a chemiluminescence NO_x analyzer (Shimadzu NOA-7000). DRIFT spectra of NO_x species adsorbed on catalysts were recorded on a Jasco FTIR-610 spectrometer equipped with a temperature-controllable diffuse reflectance reaction cell (Jasco DR600A) with a KBr window to allow *in situ* measurement under controlled gas environments at atmospheric pressure. The sample was treated in a stream of 5% H₂/He at 400 °C for 1 h and subsequently cooled down to 70 °C. After purging with He for 30 min, gas mixtures of 0.08% NO, 0–10% O₂ balanced with He was admitted to the cell for 3 h. This was followed by spectra measurement of NO_x adsorbates in a flowing He at 70 °C.

For catalytic NO–H₂–O₂ reactions, mixed gas consisting of 0.08% NO, 1–20% O₂, 0.07–0.56% H₂, balanced with He was supplied to the catalyst bed at *W/F* = 0.24 s g cm⁻³. Effluent gas was analyzed using a chemiluminescence NO_x analyzer (Shimadzu NOA-7000) and a TCD gas chromatography (Shimadzu GC-8A) with molecular sieve-5A and Porapak-Q columns.

3. Results and discussion

3.1. Physicochemical properties of Pt–HT

The XRD measurement of as prepared pristine HT as well as exchanged HT (Pt_c-HT and Pt_n-HT) exhibited a brucite-type layered structure. After heating at 600 °C in H₂, the layered structure was collapsed to yield an MgO-like phase with a low crystallinity [14,15]. Table 1 summarizes physicochemical properties of the heated products. The BET surface areas of Pt_c-HT (228 m² g⁻¹) and Pt_n-HT (177 m² g⁻¹) were higher than pristine HT (136 m² g⁻¹). As was demonstrated in our previous work [16], the reason for the higher surface area is explained by catalytic removal of interlayer nitrate in the presence of Pt, which yields two-dimensional mesopore structure of Pt–HTs in contrast to three-dimensional pores of the pristine HT. The Pt

Table 1
Physicochemical properties of HT, Pt_c-HT, and Pt_n-HT after heating at 600 °C in H₂

	HT	Pt _c -HT	Pt _n -HT
S _{BET} ^a (m ² g ⁻¹)	136	228	177
D _{Pt} ^b (%)	–	57	61
Cl ^c (μmol m ⁻²)	0	0.2	0
NO adsorption ^d (μmol m ⁻²)	2.4	1.1	2.1

^a Calculated from N₂ adsorption isotherm measured at 77 K.

^b Measured by H₂-O₂ titration at room temperature.

^c Measured by a X-ray fluorescence spectrometer (EDX).

^d Measured in a flow reactor, 0.16% NO, 10% O₂, He balance, 0.24 s g cm⁻³.

dispersion of Pt_c-HT and Pt_n-HT were 57% and 61%, respectively, indicating that the number of Pt exposed on surface is almost the same. However, Pt_c-HT contained residual amount (0.2 μmol m⁻²) of Cl⁻ originating from PtCl₆²⁻ even after heating at 600 °C in H₂. Chloride species are difficult to remove by heating in H₂.

The NO adsorption, which was measured on the basis of unit surface area at 70 °C, was more than 2 μmol m⁻² for HT and Pt_n-HT. The NO uptake should be originated from the basicity of Mg–Al oxides in the presence of O₂ [13]. The oxidative NO adsorption at low temperatures is thermodynamically favorable and is promoted by Pt [9]. Nevertheless, the amount of NO adsorption onto Pt_c-HT was only 1.1 μmol m⁻². The smaller NO adsorption is considered to be linked to the presence of

residual amounts of chloride species. It is reported that the oxidative adsorption of NO is strongly inhibited by Cl⁻, which competes to adsorb onto the base site on the oxide surface [17].

To elucidate the structure of NO_x adsorbates on these catalysts, *in situ* DRIFT spectra were recorded after treatment in streams of NO/He or NO/O₂/He mixtures at 70 °C (Fig. 1). All the spectra were referenced to that of the sample in flowing He just before exposure to NO. The adsorbed species formed on the present catalysts were assigned to chelating nitrite (1230 cm⁻¹) and nitrate (1630, 1500 and 1300 cm⁻¹) according to those reported previously [18,19]. In a flowing NO/He (Fig. 1a), a weak band due to chelating nitrite was observed at 1230 cm⁻¹ on Pt_c-HT and Pt_n-HT. The formation of chelating nitrite is usually observed for NO chemically adsorbed onto oxide anions on the surface of metal oxide. By contrast, the NO adsorption onto Pt_n-HT in the presence of O₂ yielded stronger peaks ascribable to nitrate, indicating the occurrence of oxidative adsorption of NO (b). These nitrate species were also observed on Pt_c-HT, but their peaks were much less intense. A small NO uptake onto Pt_c-HT should therefore be explained by the block of NO adsorption site by residual Cl.

X-ray adsorption measurement was next carried out to elucidate the electronic structure and chemical environment of Pt after heating at 600 °C in H₂. Fig. 2 shows normalized XANES at the Pt L_{III}-edge of Pt_c-HT, Pt_n-HT and standard samples including PtO₂, K₂PtCl₆, K₂Pt(NO₂)₄ and Pt foil. The white line at the Pt L_{III}-edge is an absorption threshold resonance attributed to the electronic transitions from 2p_{3/2} to unoccupied states above the Fermi level and is intensified with an increase in the d-band vacancies as a result of oxidation. Therefore, the white line absorption peak of Pt foil at 11562 eV gave a lower intensity, whereas K₂PtCl₆, K₂Pt(NO₂)₄ and PtO₂ yielded intensified peaks at a higher energy (11564 eV). Clearly, the white line features of Pt_c-HT and Pt_n-HT are similar to that of Pt foil, but a higher intensity of Pt_c-HT

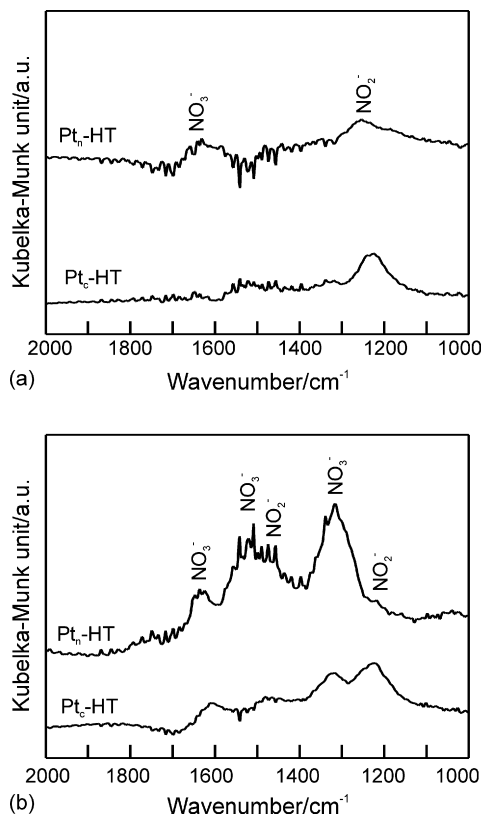


Fig. 1. *In situ* DRIFT spectra of NO_x adsorbates on Pt_c-HT and Pt_n-HT after exposing to streams of (a) 0.08% NO, He balance. (b) 0.08% NO, 10% O₂, He balance.

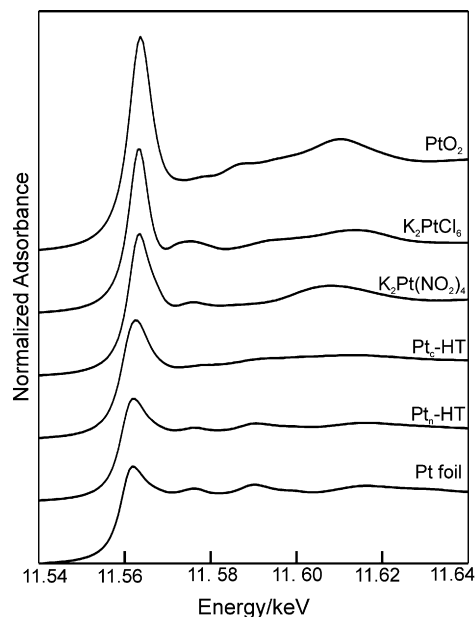


Fig. 2. Normalized Pt L_{III}-XANES spectra.

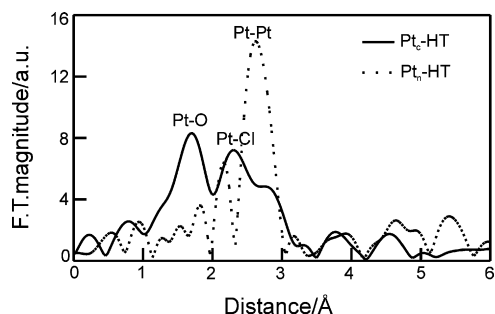


Fig. 3. Pt L_{III} edge Fourier transform EXAFS of Pt_c-HT and Pt_n-HT after heating at 600 °C in H₂.

compared to Pt_n-HT suggests the presence of a higher oxidation state Pt. This is consistent with the fact that the oscillation by XANES at higher energy side for Pt_n-HT is similar to that of Pt foil, whereas Pt_c-HT shows a very weak oscillation.

Fig. 3 shows Pt L_{III}-edge Fourier transformed EXAFS of Pt_c-HT and Pt_n-HT. The Pt_n-HT catalyst exhibited a sole peak corresponding to Pt–Pt bond with a distance of 0.27 nm. The calculated coordination number, 6.0, is less than 12 for bulk Pt. By contrast, Pt_c-HT showed three peaks due to Pt–O (0.20 nm), Pt–Cl (0.24 nm) as well as Pt–Pt (0.27 nm) bonds. The Pt–Cl bond in Pt_c-HT is longer than that in K₂PtCl₆ (0.23 nm). The Pt–Cl bond is known to extend with a decrease of the oxidation number of Pt from 0.232 nm (Pt⁴⁺–Cl) to 0.236 nm (Pt²⁺–Cl) [20,21]. The calculated coordination numbers, 1.5(Pt–O), 0.8(Pt–Cl) and 1.8(Pt–Pt), are very small probably because Pt species bound to different numbers of residual chloride. In such a case, the coordination number of Pt–Pt shell is very difficult to estimate by the curve-fitting of FT-EXAFS oscillation. These results of XANES and EXAFS analysis suggest that Pt in Pt_c-HT was partly oxidized (PtCl_xO_y) due to residual chloride strongly bound to Pt even after heating at 600 °C in a H₂ flow.

3.2. Catalytic properties of Pt-HT for NO–H₂–O₂ reaction

The catalytic property of Pt_c-HT and Pt_n-HT for the NO–H₂–O₂ reaction was measured in a flow of 0.08% NO, 10% O₂, 0.28% H₂, balanced with He. Fig. 4 shows NO/H₂ conversions and N₂/N₂O selectivities in the temperature range of 50–130 °C. The NO_x conversion over Pt_c-HT was observed at ≥50 °C. An increase in the reaction temperature led to a significant increase in the NO_x conversion, which gave rise to the maximum, 83%, at 70 °C. The agreement between light-off curves of H₂ and NO implies that H₂ cannot be consumed by simple H₂–O₂ reaction but the NO–H₂ reaction is dominant at low temperatures. At higher temperatures, however, the NO_x conversion was decreased monotonously, whereas H₂ conversion remained 100%. The decreasing NO_x conversion can be explained by the fact that NO and O₂ compete to react with H₂. The NO/H₂ conversions of Pt_n-HT were comparable with that of Pt_c-HT. This is reasonable, considering the almost same BET surface area and Pt dispersion of these two catalysts. However, it should be noted that the N₂/N₂O selectivity was

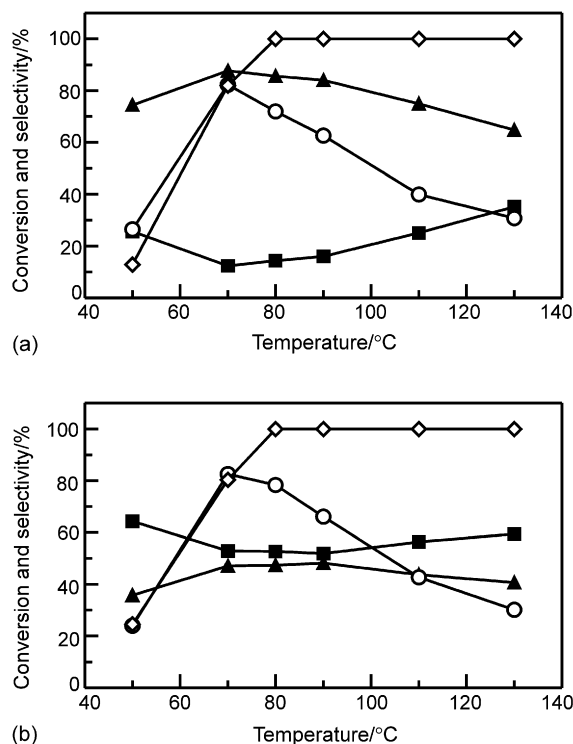


Fig. 4. Conversion and selectivity of (a) Pt_c-HT and (b) Pt_n-HT. (○) NO_x conversion, (◇) H₂ conversion, (■) N₂ selectivity, (▲) N₂O selectivity. 0.08% NO, 10% O₂, 0.28% H₂, balanced with He, W/F = 0.24 s g cm⁻³.

significantly different between Pt_c-HT and Pt_n-HT. In the present catalytic reactions, N₂ and N₂O formed as main products, but NH₃ was not detected. The N₂ selectivity of Pt_c-HT was only 12% at 70 °C, where maximal NO_x conversion was obtained, whereas that of Pt_n-HT was 53% at the same temperature. The higher selectivity to N₂O relative to N₂ for Pt_c-HT causes a serious problem, because increasing attention is now given in avoiding the formation of this greenhouse gas.

Fig. 5 shows the effects of O₂ and H₂ concentrations in the gas feed on the NO_x conversion and N₂ selectivity at 70 °C. Considering the competitive H₂–O₂ reaction, the NO–H₂ conversion is expected to decrease at higher O₂ concentrations. Actually, however, the two catalysts exhibited quite different behaviors as shown in Fig. 5a, i.e., NO_x conversion of Pt_c-HT was decreased with an increase of O₂ much more than that of Pt_n-HT. The Pt_n-HT catalyst could therefore keep twice as high NO_x conversion as Pt_c-HT at 20% O₂. More interestingly, the N₂ selectivity of Pt_n-HT increased with an increase of O₂. This simply means that more H₂ would be selectively consumed by the reaction with NO. On the other hand, the NO_x conversion of both catalysts increased monotonically with H₂ concentration (Fig. 5b). Pt_n-HT exhibited again higher activities compared to Pt_c-HT. Irrespective of incremental H₂ concentration, the N₂ selectivity of both catalysts was kept almost constant.

The high selectivity to N₂O of Pt_c-HT is similar to that of Pt catalysts supported on acidic oxides such as SiO₂ and ZSM-5 [6,8]. According to our previous work [8], the addition of Lewis base like Na greatly improves the N₂ selectivity of Pt–ZSM-5, because Na promotes the adsorption of NO as NO₂⁻-type

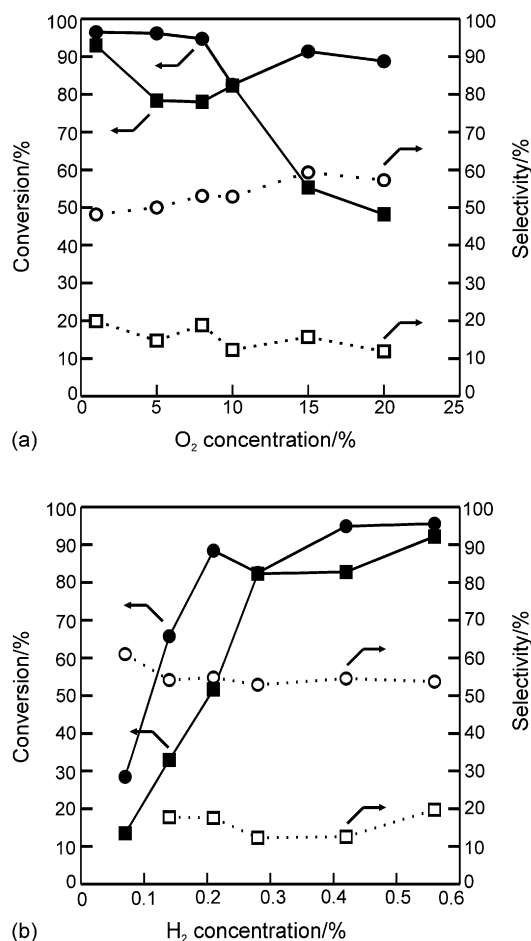
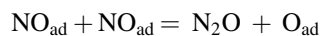


Fig. 5. Effects of (a) O₂ concentration and (b) H₂ concentration on NO_x conversion and N₂ selectivity at 70 °C. Pt_c-HT; (■) NO_x conversion and (□) N₂ selectivity. Pt_n-HT; (●) NO_x conversion and (○) N₂ selectivity. 0.08% NO, 1–20% O₂, 0.07–0.56% H₂, balanced with He, W/F = 0.24 s g cm⁻³.

species, which would play a role of an intermediate to yield N₂. In the Pt_c-HT catalyst, such an oxidative NO adsorption is suppressed by the residual chloride strongly bound to Pt (Table 1). According to the mechanism proposed by Burch and Coleman [5], the formation of N₂O in the NO–H₂–O₂ mixture forms as follows,



In the present system, chloride bound to Pt in Pt_c-HT would suppress the adsorption as NO₂/NO₃ and thus increase the NO-type species, which lead to the formation of N₂O.

By contrast, a large amount of NO adsorption occurred onto the catalyst prepared from Pt_n-HT, where NO₂/NO₃ species were observed by *in situ* FT-IR (Fig. 1). It is difficult to distinguish between NO_x species adsorbed on Pt and those on the support because the Pt-loaded and unloaded HT gave almost similar spectra. We thus consider that NO₂/NO₃ species were formed not only on the support but also on Pt. This can be supported by the fact that NO_x conversion was less dependent on the O₂ concentration in the gas feed (Fig. 5a). NO adsorbed as NO₂/NO₃ should monopolize Pt surface and thus severely limits simple H₂–O₂ reaction at lower temperatures. Increased

amount of NO₂/NO₃ on the Pt surface should also limit the formation of N₂O *via* the reaction route shown above. These oxidized NO adsorbates may not be stable at increasing H₂ concentrations. This is consistent with Fig. 5b, where N₂ selectivity was not improved by increasing the H₂ concentration in the gas feed. Furthermore, it was implied that NO_x adsorbed on the support takes part in the reaction with H₂. Since hydrogen spillover was not observed in the present system, the NO_x species on the perimeter site surrounding Pt would play a key role in such processes. More studies on the role of adsorbed NO_x species in NO–H₂–O₂ reactions over Pt_n-HT are now under investigation.

4. Conclusion

In the present work, Mg–Al oxides supported Pt catalysts, Pt_c-HT and Pt_n-HT, which were prepared from PtCl₆²⁻ and Pt(NO₂)₄²⁻-exchanged hydrotalcites, respectively, were applied to NO–H₂–O₂ reaction at low temperature (≤130 °C). Although the BET surface area and Pt dispersion of the two catalysts after heating at 600 °C in H₂ were similar, Pt_n-HT showed much higher N₂ selectivity of 53%, whereas Pt_c-HT was more selective to N₂O (87%). The high N₂ selectivity can be explained by the NO reduction route *via* oxidative adsorption as NO₂/NO₃ intermediate. The EXAFS analysis demonstrated that the presence of Pt–Cl and Pt–O bonds in the Pt_c-HT catalyst, whereas only a Pt–Pt bond present in the Pt_n-HT. The oxidative NO adsorption should therefore be inhibited by the residual chloride species, which block the base site on the surface of HT-derived Mg–Al oxides.

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